Lungren.

A Study Of The Chemical Structure
Of The Compounds In Coal



A STUDY OF THE CHEMICAL STRUCTURE OF THE COMPOUNDS IN COAL

ву

EDGAR EMMANUEL LUNGREN

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A STUDY OF THE CHEMICAL STRUCTURE OF THE COMPOUNDS IN COAL

 $\mathbf{B}\mathbf{Y}$

EDGAR EMMANUEL LUNGREN

The

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

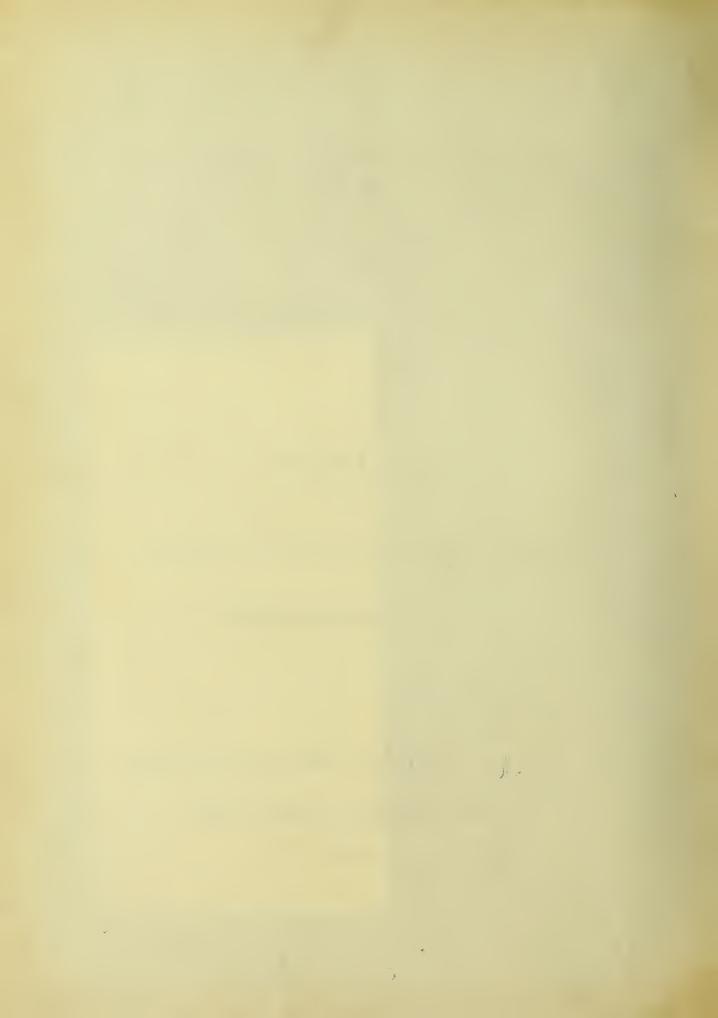
IN

CHEMICAL ENGINEERING

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1915



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IN COAL

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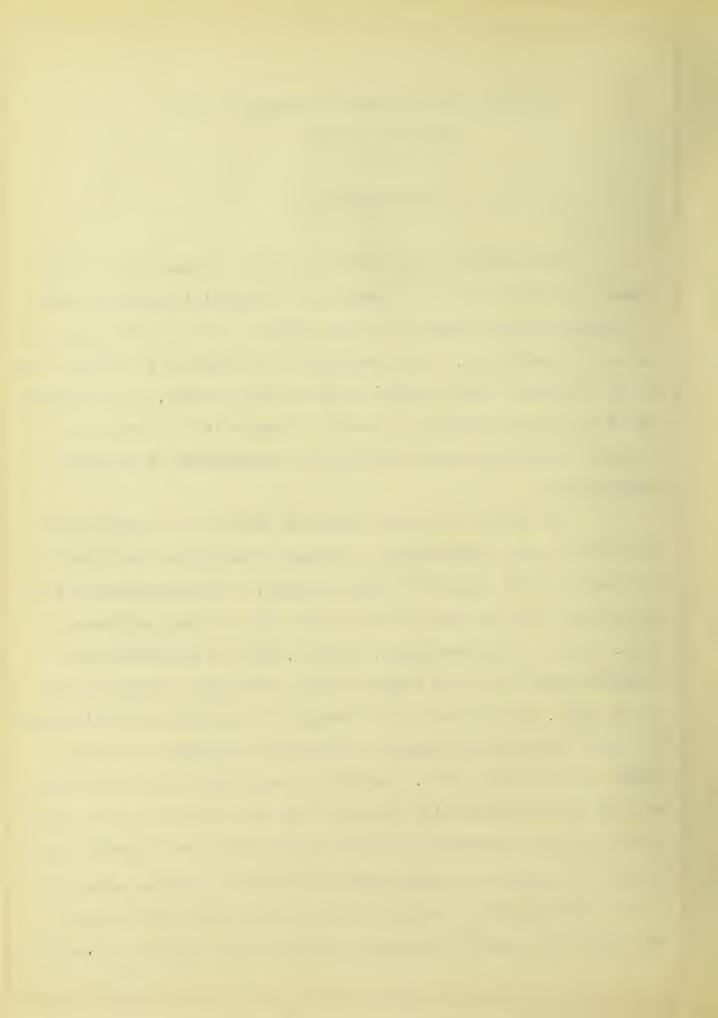


A STUDY OF THE CHEMICAL STRUCTURE OF THE COMPOUNDS IN COAL

INTRODUCTION

Any investigation which may tend to throw light on the chemical nature of coal is justified by scientific interest which is always centered about the determination of the constituents of an unknown substance. The development of methods for treating coal so as to improve the products of the coking process, or of methods for the direct production of energy by means of fuel cells can hardly be expected until the chemical constituents of coal are better known.

In spite of the fact that the study of the composition of coal has been undertaken by numerous investigators and that the subject has been attacked by many methods, it is nevertheless true that very little is known of the true nature of the substances in coal. This is not remarkable, however, when we consider what a complex composition coal seems to have according to present data. In the past, various methods of vacuum and destructive distillation have been carried out without lending much knowledge as to the nature of the coal itself. Methods of separating the constituents of coal by extraction with solvents have been used, and it is only recently that successful results have been obtained by such a procedure. The present outlook seems to indicate that the extension of the investigation along the line of extraction with solvents



and perhaps definite chemical compounds.

If, then, such compounds are isolated, we may not be certain that they existed as such in the coal originally; for, not knowing the composition of the coal, it is not wise to say that the action of the solvents does not cause chemical rearrangement. It is known, however, that the physical properties of coal do change when it is exposed to abnormal conditions such as high temperature and excessive weathering.

Having isolated simpler substances from coal, it seems plausible to assume that they should respond to the same characteristic tests whether in the free state or bound up in the coal substance. A series of tests on coal for groups known to exist in the isolated compound would serve as a means of determining the extent of chemical reaction during extraction. It was with this point in view that the present work was begun.

The purpose of the work was to determine the existence of certain characteristic organic groups in coal, paying particular attention to the way in which oxygen is combined. Interest centers about the element oxygen because of the fact that such large quantities are absorbed by coal from the atmosphere. Previous experiments have pointed to the supposition that oxygen is chemically combined in coal in the form of the hydroxyl group. This paper gives an account of the experiments that were carried on to determine the presence of the hydroxyl group in coal.



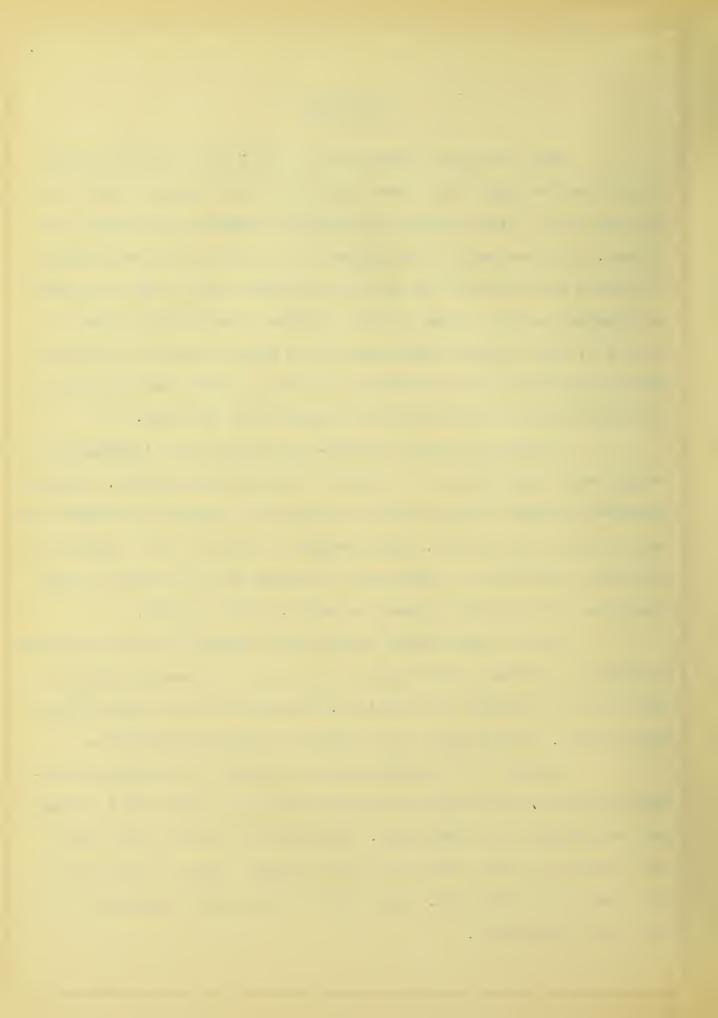
HISTORICAL

The spontaneous combustion of coal under certain normal conditions has long been known, and it has been supposed that this was due to the slow action of atmospheric oxygen on the coal substance. This assumption was proven to be true by the experiments of Porter and Ralston $\frac{1}{2}$ in which they showed that an 80 gr. sample of Wyoming coal in a bath of 42° C. caused a temperature rise of over 6° C. when treated with oxygen in a sealed tube for two hours. They interpreted this exothermic reaction as being due in part to the oxidation of the unsaturated compounds in the coal.

As early as 1868 Richters $\frac{2}{3}$ noted that coal increased in weight when maintained at a slightly elevated temperature. Jazukowitsch $\frac{3}{3}$ confirmed this in 1879 by noting the increase in weight due to heating coal at 120° C. Experiments by \cos^4 in which samples of coal were sealed in an atmosphere of oxygen for two months showed that some coals would increase as much as 2% in weight.

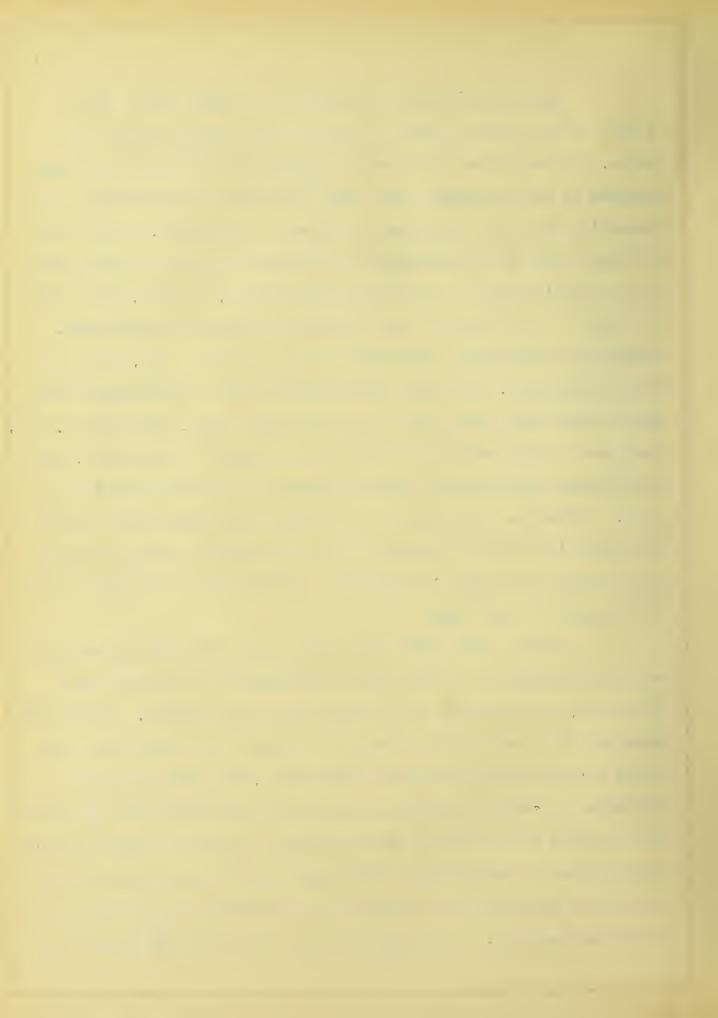
Further experiments by Parr and Wheeler in which the gas contained in Putnam jars which had held coal for several months was found by analysis to contain 1.5% oxygen and less than 2% carbon dioxide, strengthened the evidence of oxygen absorption.

Winmill and Graham actually measured the volume of oxygen absorbed by dry and wet samples of coal and found that oxidation was not complete in sixty days. They noted that the same amount was absorbed in each case, but that a longer time was required in the case of the wet coal. The rate of absorption increased rapidly with the temperature.



That weathering or absorption of oxygen has a great effect on the value of coal is shown by the change in heating value. It was shown in the work of Cox that coal which had been exposed to air or oxygen lost from 2 to 10% of its calorific value depending upon the origin and fineness of the sample. Coal which had been kept in an atmosphere of nitrogen or carbon dioxide showed no deterioration. It must be kept in mind, however, that calorific loss is due in part to the escape of volatile hydrocarbons. Porter and Ovitz have shown that there is such a loss, but that it is very small. In other experiments these investigators have shown that fifty pound portions of New River coal, one-half in size, lost none of its calorific value when submerged in sea-water, but that three hundred pound samples exposed to the air lost 1% in a year. White has shown that coals having high oxygen and low ash contents will have very nearly the same calorific value as coals of low oxygen and high ash contents, provided that the total carbon is the same in each case.

It is a well established fact that coals will lose their coking property to a large extent when exposed to the air for a long time, or if heated for a short time to 200°-300°C. Bouduard 10° observed that coal which had been so treated contained humic acid which did not exist in the coal originally, and which could be separated by extraction with a sodium hydroxide solution. He found the presence of humic acid wherever there had been a loss of coking property due to weathering. The humic acid thus obtained was very similar to that which is formed by the condensation and dehydration of polysaccharides. In continuing the work Bouduard 11° found that

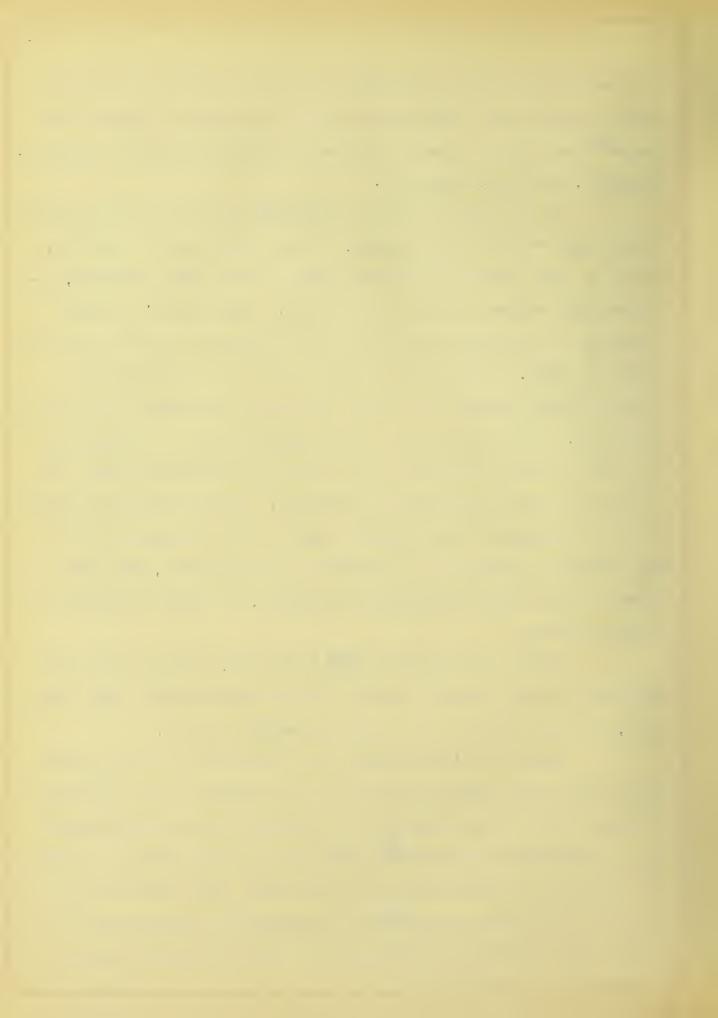


the composition of the extracted humic acid checked very closely with formulae which had previously been proposed by Bertholet and Andre $\frac{12}{2}$ and others. These formulae are given as follows: $C_{18}H_{14}O_{6}$, $C_{18}H_{18}O_{9}$, $C_{18}H_{14}O_{9}$, $C_{18}H_{14}O_{11}$.

In the work of Parr and Hadley in which various Illinois coals were extracted with phenol, it was found that the extract, which is that part of coal which gives it the coking property, absorbed less oxygen than did the residue. Moreover, the coking property of the extract was but little impaired by heating for 120 hours at 105°C. In the case of the residue the comparatively slight coking property was almost completely destroyed by the same treatment. They concluded that the oxygen which was absorbed by the coal, residue and extract was chemically combined rather than being in a state of mechanical occlusion, because oxidation produced (1) a lowering of the volatile matter and an increase in the CO₂ content of the gases of destructive distillation, (2) a decrease in the amount extractable by phenol, and (3) a decrease in coking property.

Erdmann and Stolzenberg have shown further that weathered coal gives a smaller amount of tar on distillation than fresh coal, but that the tar has a higher paraffin content.

Nearly all investigators who have worked on the subject believe that the oxygen absorbed by coal combines with unsaturated compounds which then decompose to a smaller extent giving $\rm CO_2$ and $\rm H_2O$. Hillebrand and Badger 15 offered such an explanation as cause for errors in the determination of moisture. This has been confirmed in the work of Mahler 16 and Taffenel 17 . The absorption of oxygen with consequent splitting off of carbon dioxide explains the



phenomenon which was noted in the work of $Cox^{\frac{4}{3}}$, namely, a rapid fall of the pressure in the apparatus in which coal was being treated with oxygen, followed by a slight rise in the pressure.

Parr and Kressman 18 have shown that when samples of various coals are heated in a current of oxygen, the evolution of carbon dioxide is indicated at a temperature near 120°C. in every case.

Porter and Ralston have shown that although carbon dioxide evolution is subsequent to oxidation, the amount of carbon dioxide given off is less than .Ol of the amount of oxygen absorbed.

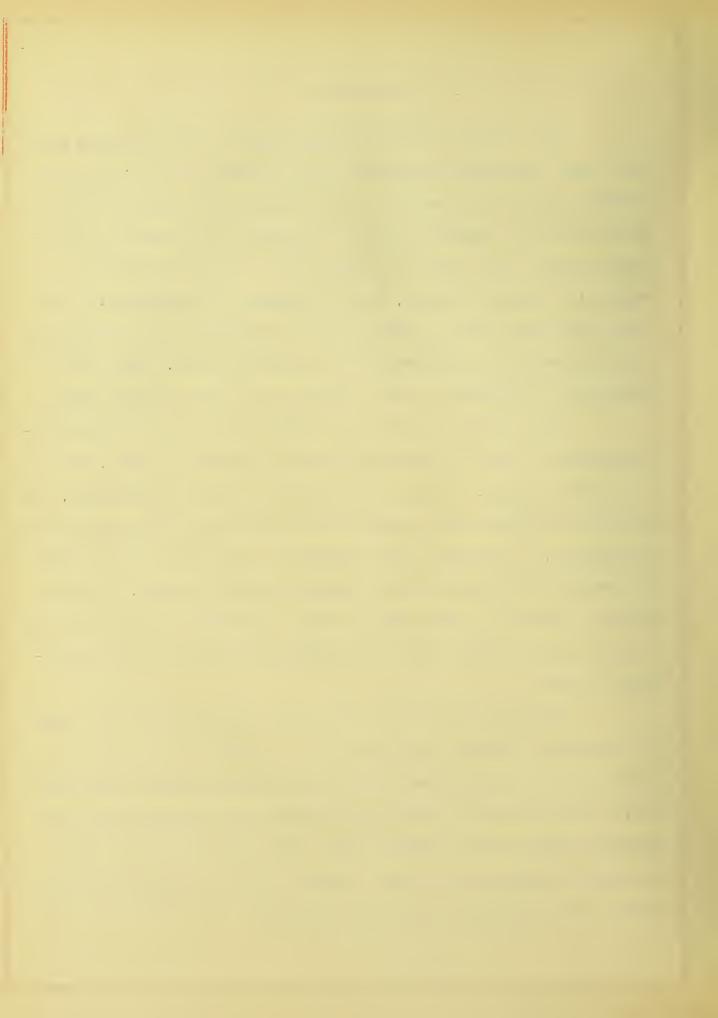


EXPERIMENTAL

The results of the work mentioned in the foregoing pages give almost conclusive evidence that at least part of the oxygen absorbed by coal is chemically held. There are reasons to believe that part of the oxygen so held is present in the form of the hydroxyl group since that is a common form of the combination of oxygen in vegetable matter, as for instance, in cellulose. The fact that humic acid is always found in weathered coal strengthens the evidence of the presence of the hydroxyl group, since such a structure is essential in the constitution of any organic acid.

The present work was undertaken with a view to determining whether or not the hydroxyl group was present in coal, and if so, to what extent. Since difficulties have been encountered, the work has developed into a search for a method of making such a determination. Previously, the compounds in coal have been studied by vacuum distillation and by extraction with solvents. It has been the purpose of this work to study the effect of treating coal directly with reagents which are characteristic tests for the hydroxyl group.

Three general methods have been carried out with a view of determining whether the substances in coal will react with benzoyl chloride, phosphorus trichloride and phosphorus pentachloride. The reaction in each case consists of the replacement of a hydroxyl group by one chlorine atom, with the formation of one molecule of hydrogen chloride. In the case of a compound such as phenol, the reactions would be as follows:



 C_6 H_5 $COC1 + C_6H_5OH = C_6$ H_5 $COOC_6$ H_5 + HC1P Cl_3 + C_6 H_5 OH = C_6 H_5 Cl + P O Cl + H Cl

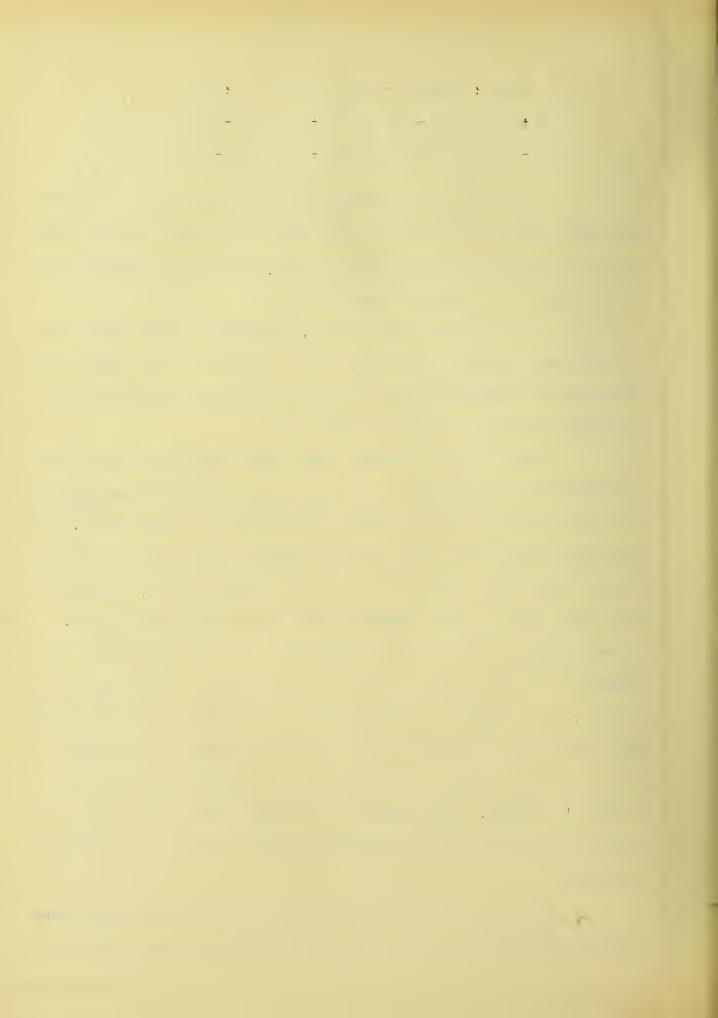
 $P Cl_5 + C_6 H_5 OH = C_6 H_5 Cl + P O Cl_3 + H Cl$

It must be remembered, however, that water will react in the same way as does phenol, and that such a reaction with the moisture of the coal must not be interpreted as an indication of the presence of a hydroxy compound.

In the first method used, thoroughly dried coal was treated with benzoyl chloride, and the extent of the reaction determined by collecting the volatilized hydrogen chloride in a standard solution of sodium hydroxide.

In the second method, oven dried samples of coal were treated with phosphorus trichloride and phosphorus pentachloride, the excess of the reagent being decomposed by adding water. If a hydroxyl group were present in an aromatic compound or in an aliphatic compound having a long chain of carbon atoms, the resulting chloride formed by the reaction would probably be insoluble. Hence, by washing the coal substance free from soluble chlorides, the organic chloride would be left in the residue. After washing and drying, the residue was decomposed by combustion in a Parr Sulphur Cup with sodium peroxide as the oxidizing agent. The residue was then dissolved and the chlorine in the solution determined by Volhard's method. The amount of chlorine found would thus be proportional to the amount of hydroxyl group present in the coal originally.

In the third method, coal was treated with phosphorus pentachloride, and after the reaction had ceased the excess of re-



agent was decomposed by adding water. Hydrogen chloride evolved during the process was collected and returned to the coal mixture. The mixture was then made up to standard volume and aliquot portions were analyzed for hydrochloric and phosphoric acids.

The ultimate decomposition of phosphorus pentachloride with water results in the formation of hydrochloric and phosphoric acids as follows:

$$P Cl_5 + 4 H_2 O = 5 H Cl + H_3 PO_4$$

A known amount of phosphorus pentachloride will produce a known amount of each of the two acids. In this experiment a decrease in the amount of hydrochloric acid would indicate that some of the chlorine had replaced the hydroxyl group in the organic substance of the coal and hence would not be effected during the titrations with sodium hydroxide. Therefore, the hypothesis is that the difference between the theoretical yield of hydrochloric acid and the amount actually found in the coal mixture would be proportional to the amount of the hydroxyl group present in the coal substance.

The coal used in all of the experiments was a sample of screenings of a good grade of Illinois coal. Fuel Lab. No. 7922.

Analysis of coal as received

Moisture 12.34 %

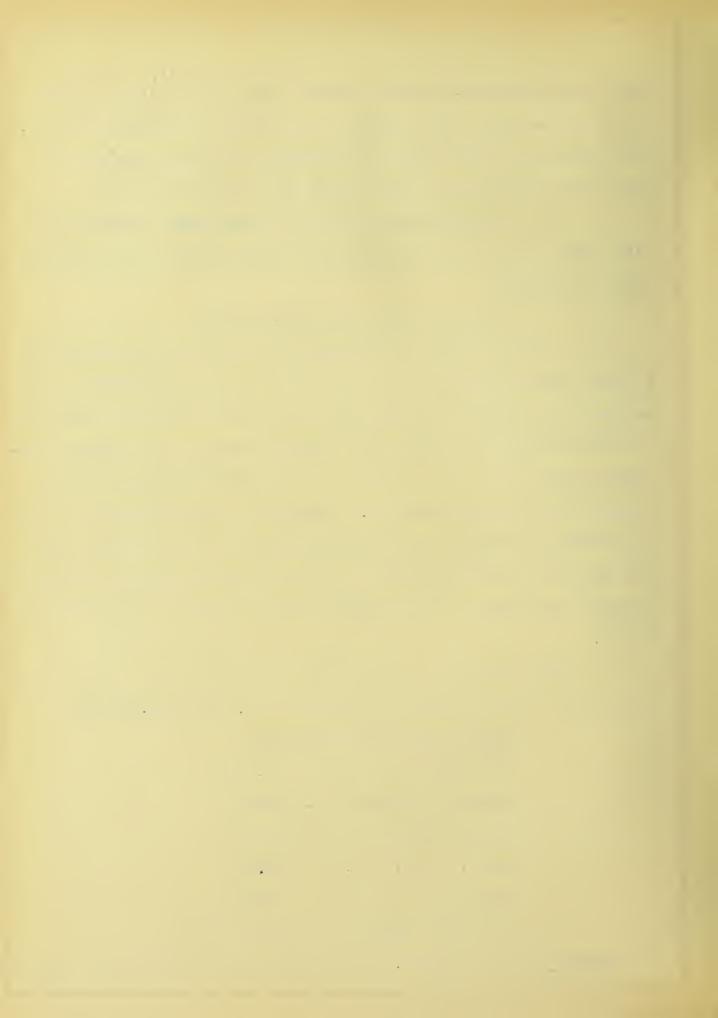
Volatile Matter 35.87

Fixed Carbon 37.97

Sulphur 3.45

Calorific Value 10,542 B.t.u.

Method 1 (a) A 100 cc. Florence flask was fitted with a sep-

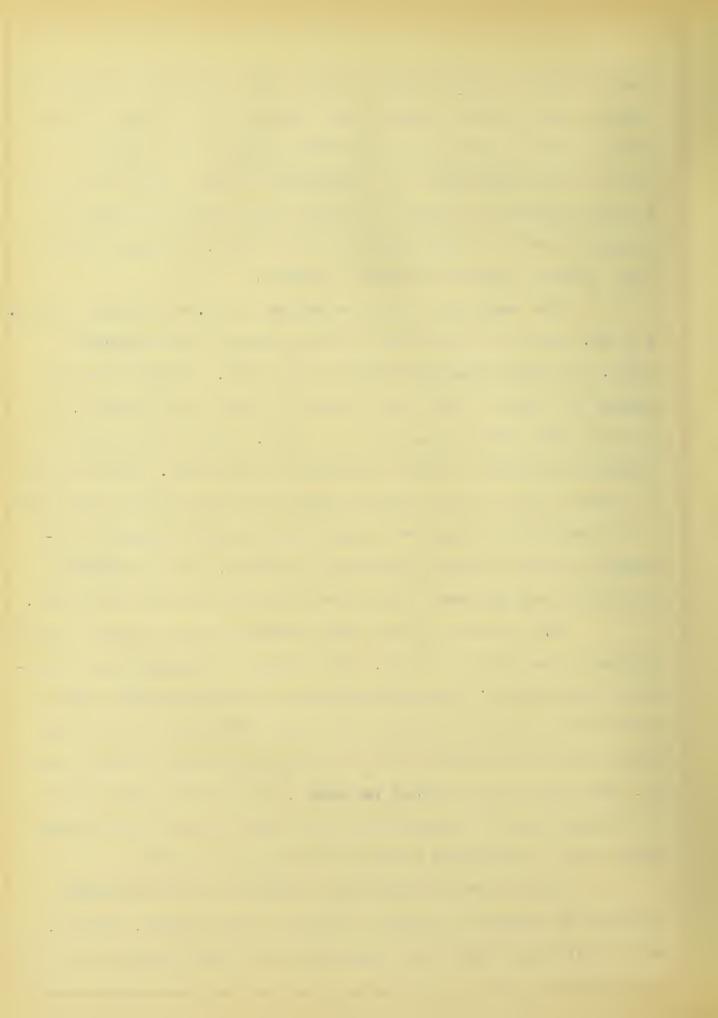


aratory funnel, a short glass delivery tube, and another glass tube leading nearly to the bottom of the flask. The delivery tube was connected with another tube which was immersed in a standard solution of sodium hydroxide in an Erlenmeyer flask. Hydrogen made in a Kipp generator was freed of hydrogen chloride and moisture by passing through a sodium hydroxide wash bottle, a calcium chloride tube, and two sulphuric acid wash bottles.

The separatory funnel contained 10 cc. of benzoyl chlorida. A 10 gr. sample of oven-dried coal was placed in the Florence flask. To effect thorough drying of the coal, the flask was immersed in a bath at 103°C. and heated for one hour in vacuuo, the delivery tube being connected with a pump. Then a slow stream of hydrogen was passed through the flask for two hours. After drying the coal in this way the delivery tube was closed and the stop-cock of the separatory funnel was opened just enough to allow the hydrogen to bubble through the benzoyl chloride, for the purpose of driving out any hydrogen chloride which might be held in solution.

The heating bath was then removed and the benzoyl chloride allowed to run into the flask. The passage of hydrogen was continued for two hours in order that evolved hydrogen chloride might be carried over into the alkaline solution. Titration of the sodium hydroxide solution showed that no hydrogen chloride had been evolved. The experiment was then repeated, but with the same result. If benzoyl chloride did react with the coal it was to such a small extent that the hydrogen chloride was held in solution.

(b) The same procedure was repeated using phosphorus trichloride instead of benzoyl chloride. This reagent, however, was so volatile itself that quantities of it were carried over and



the alkaline solution was quickly neutralized.

Method 2. As described above, the procedure in this method consisted of the treatment of coal with (a) phosphorus trichloride and (b) phosphorus pentachloride, and the determination of chlorine in the washed dried residue.

(a) 10 grs. of the oven-dried coal was placed in a 100 cc. Florence flask with 50 cc. of phosphorus trichloride, and the flask was connected with a reflux condenser by means of a ground glass connection. To effect a thorough reaction, the flask was placed on a water-bath and the mixture allowed to boil. Samples for analysis were taken out at the end of 3-1/2, 17-1/2 and 25 hours.

The excess of phosphorus trichloride was decomposed by adding water, and after boiling, the mixture was filtered. The residue on the filter was washed with boiling water until the filtrate showed no test for chlorides, and it was then dried in the oven for one hour at 105°C. The appearance of the dried residue was but little different from that of the coal originally, having perhaps a slightly browner shade.

0.5 gr. of the residue was mixed with 10 grs. of sodium peroxide in a Parr Sulphur Cup and combustion started by heating over a Bunsen burner. The fusion was dissolved in warm distilled water and after acidifying with nitric acid, the solution was filtered. The chlorine content of the solution was determined by Volhard's method according to the modification of Rothmund and Burgstaller 19. This method consists of titration with standard solutions of silver nitrate and potassium sulphocyanate, using a ferric alum solution as the indicator. The results of the analyses are

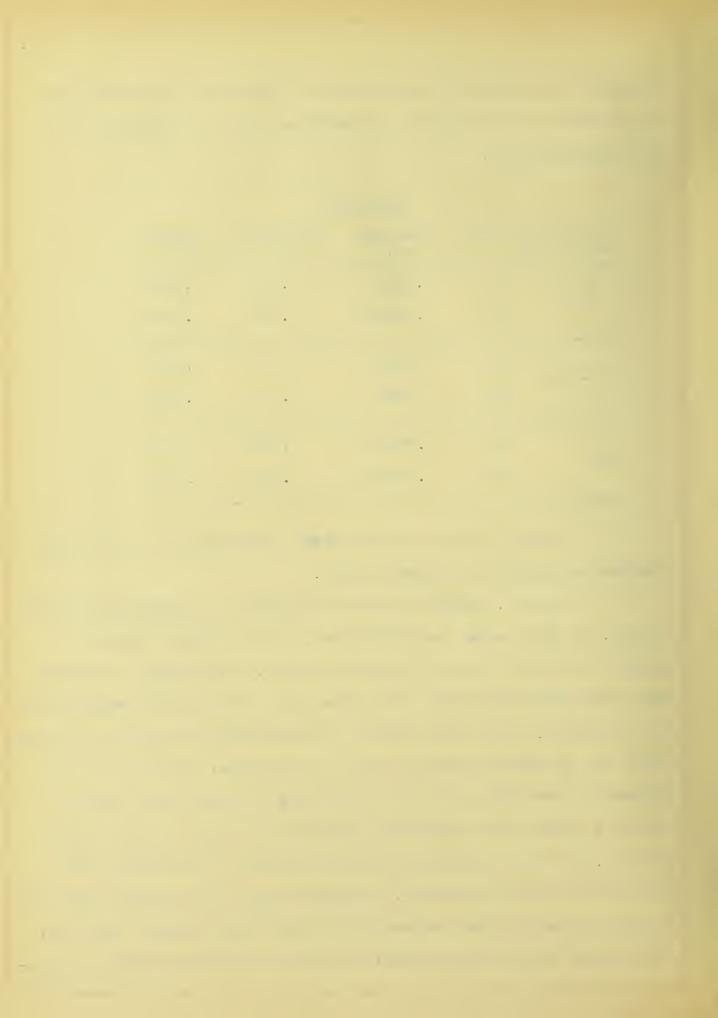


tabulated below with the percentages of oxygen on the basis that the presence of chlorine in the residue is due to replacement of the hydroxyl group.

Results						
Hours of boiling with P Cl ₃		Chlorine gr.	Chlorine %	Oxygen %		
3-1/2	(1)	.0023	.46	.208		
υ - 1/2	(2)	.00235	.47	.212		
17-1/2	(1)	.00301	.60	.271		
11-1/2	(2)	.0027	• 54	. 244		
25	(1)	.00248	.496	.224		
20	(2)	.00242	.484	.218		

(b) The action of phosphorus pentachloride on coal was studied according to the same method.

A 10 gr. sample of coal was ground in a mortar with about 10 grs. of phosphorus pentachloride and the mixture allowed to stand in a bottle over Ca Cl₂ for 24 hours. The excess of reagent was decomposed with water, the mixture was filtered and washed with boiling water, but it was found to be practically impossible to wash until the filtrate showed no test for chlorides. Several methods of washing were used, such as boiling the residue with a large volume of water, and continuous agitation by means of an electric stirrer, but the filtrate showed the presence of chlorides even after days of such treatment. Obviously then, this method could not be used, since the coal showed such avidity for hydrogen chloride. This result led to the conclusion that the chlorides found by analy-



in (a) were likewise mechanically occluded rather than chemically combined.

Method 3. This method consisted of the treatment of coal with phosphorus pentachloride, decomposition of the excess with water and the determination of hydrochloric and phosphoric acids in the solution thus obtained. Instead of filtering and trying to wash the residue free of H Cl as in Method 2, the solution containing the coal residue in suspension was titrated directly with sodium hydroxide for the two acids. In such a case even if either or both of the acids were occluded by the coal they would likely react with the sodium hydroxide during titration.

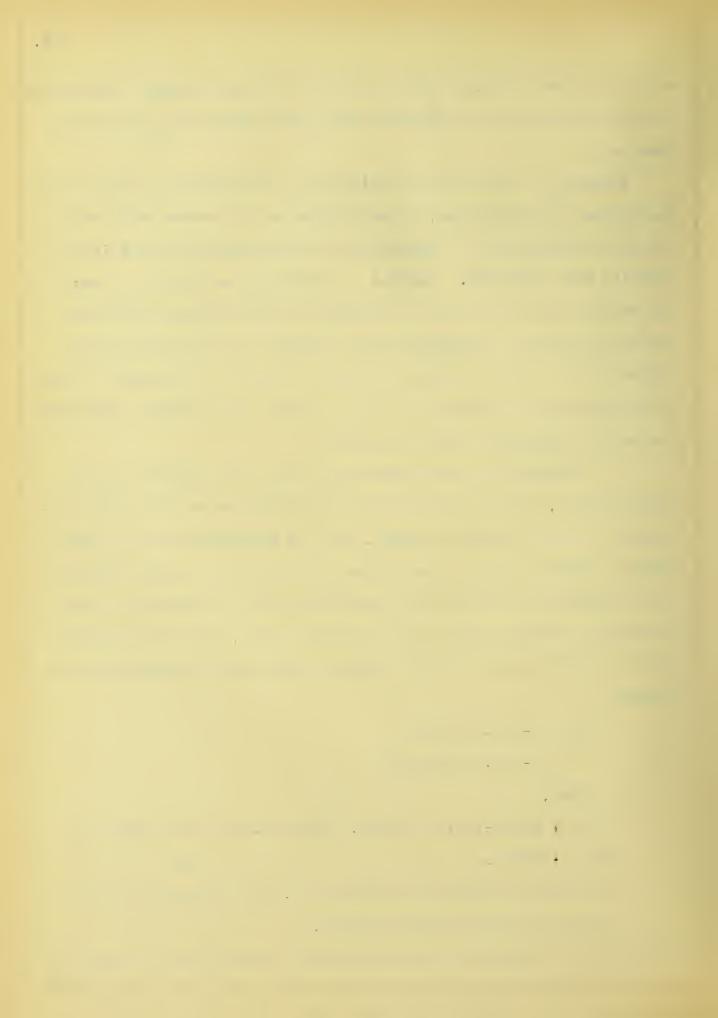
Hydrochloric and phosphoric acids, when present in the same solution, may be determined by titrating twice with sodium hydroxide, using (1) methyl orange, and (2) phenolphthalein as indicators. Methyl orange is sensitive to but one equivalent hydrogen ion in phosphoric acid, while phenolphthalein is sensitive to two equivalent hydrogen ions. It is evident, then, that two equations could be obtained and the two unknown acids could be determined as follows:

Let X = cc. of H Cl Y = cc. of $H_3 PO_4$ Then.

- (1) X + 1/3Y = cc. of stand. NaOH req. for 1st titration
- (2) X + 2/3Y = " " " " " 2nd "

Solving for X and Y we get the cc. of H Cl and ${\rm H}_3$ PO $_4$ in terms of the normality of NaOH.

This method of analysis is not absolutely correct, but the error is



constant and it is accounted for in the blank test.

Known amounts of the two acids were titrated in the presence of one gram samples of powdered coal in about 200 cc. of water. In each case the amount of phosphoric acid indicated was greater, and the amount of hydrochloric acid was smaller than the known amounts, but the discrepancy appeared to be quite constant. The average of a series of determinations gives a fairly accurate value of the constant:

Results

No.	Known	Amounts	By Analysis
	cc. H ₃ PO ₄ .831 N	.60 N	cc. H ₃ PO ₄ cc. H Cl .831 N .60 N
1.	5.70	14.86	8.20 12.16
2.	7.15	12.04	9.98 9.14
3.	3.49	12.65	5.60 10.14
4.	4.50	13.36	7.11 10.50
5.	3.96	13.46	6.44 10.90
6.	5.25	8.49	7.09 6.07
7.	4.70	11.80	7.36 8.93
8.	5.71	12.30	8.29 9.76
9.	5.50	10.76	7.96 8.12
Average	5.106	11.08	7.56 9.52
Average in cc. at 1.N	4.25	6.65	6.29 5.71

Increase in amount of H3 PO4 = 2.04 cc.

Decrease " " H Cl = .94 cc.

It is not within the scope of this paper to account for

the discrepancy, but it is likely that the calcium carbonate in coal is more readily attacked by hydrochloric acid than by phosphoric acid. Suffice it to say that these preliminary tests showed the necessity of running blank tests.

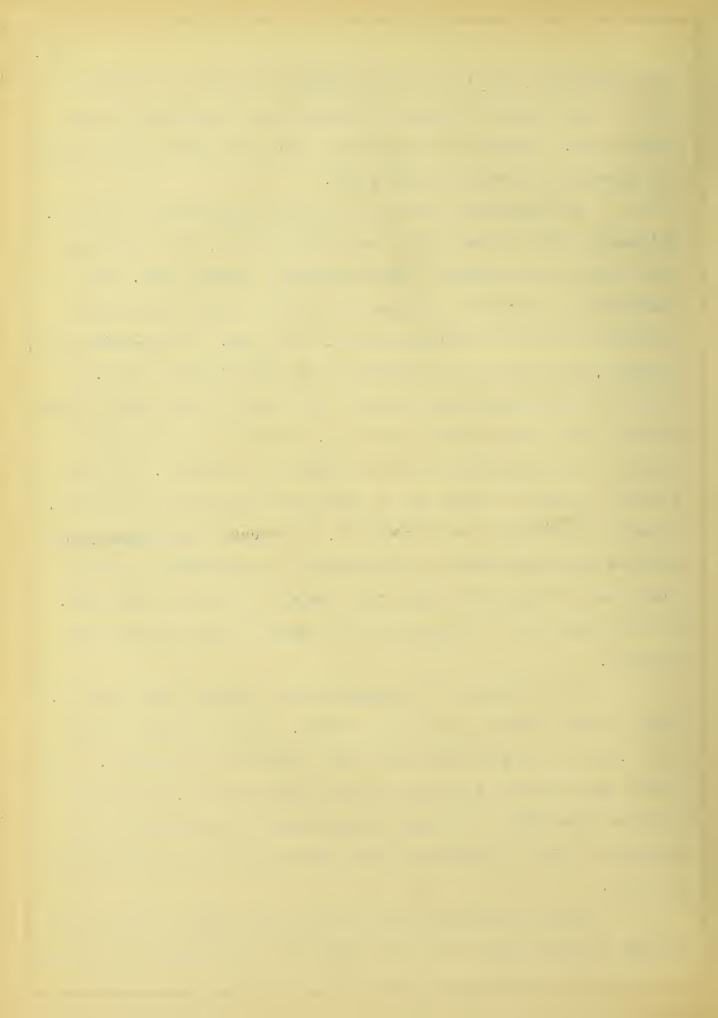
The apparatus used in this method consisted of a 250 cc.

Erlenmeyer flask fitted with a separatory funnel, and a delivery tube which led into another flask through a mercury seal. The second flask contained a standard solution of sodium hydroxide.

The first flask was thoroughly dried, and 2 grs. of oven-dried coal, 100 mesh, was placed in it together with approximately 2 grs. of powdered phosphorus pentachloride. The stopper was quickly placed and the flask shaken quite vigorously. Evolution of gas and a slight rise in temperature gave evidence of a reaction. The mixture was allowed to stand for 24 hours, with shaking at intervals. Assuming the reaction to be complete, the excess phosphorus pentachloride was decomposed and the gaseous H Cl dissolved by adding enough water through the separatory funnel to fill the apparatus. By this scheme all the products of the reaction were obtained in solution.

The contents of the apparatus were washed into a 100 cc. flask and the solution made up to volume. After vigorous shaking 200 cc. of the mixture was drawn with a pipette for analysis. This sample was heated to boiling to expel carbon dioxide, and was then titrated twice with a standard sodium hydroxide solution for hydrochloric acid and phosphoric acid according to the method described above.

Blank tests were made by decomposing about 2 grs. of phosphorus pentachloride in the same apparatus, and making the solution



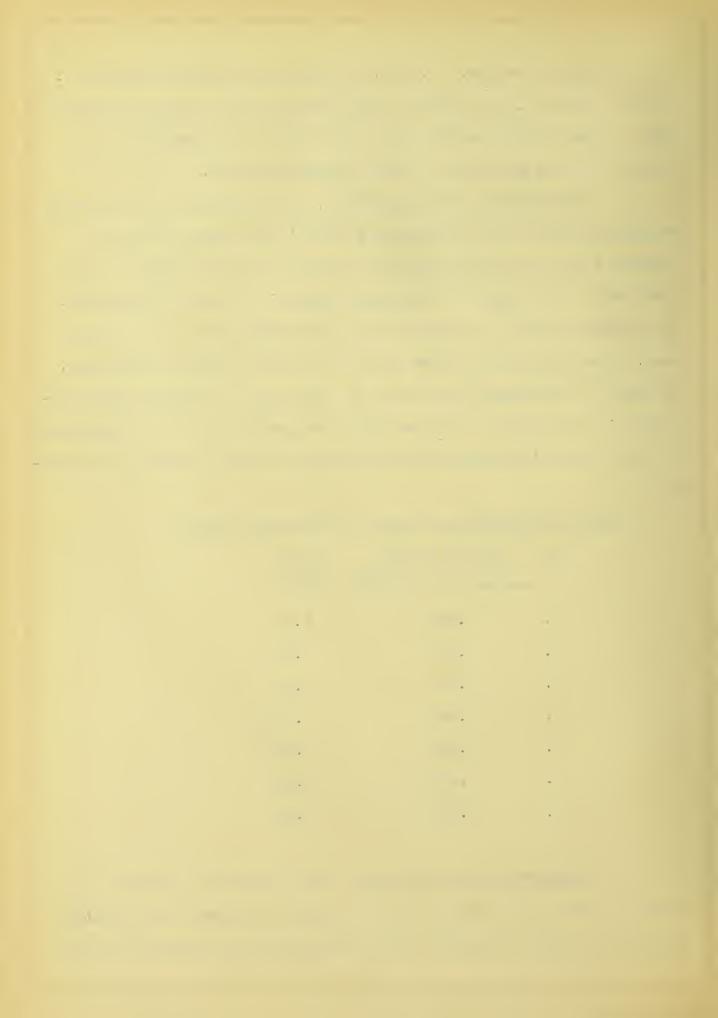
up to volume as before. 0.4 gr. of coal was treated with 200 cc. of this solution, the mixture being heated to boiling and titrated. Such a blank should account for variations in the purity of the reagent and for meactions of the two acids on coal.

According to the hypothesis, the difference in the ratios of hydrochloric acid to phosphoric acid in the case of direct treatment of coal with P Cl₅ and in the blank test should be proportional to the amount of hydroxyl group in the coal originally. As a matter of fact, no appreciable difference was found in any case. The tabulations below show the ratios found in some cases. It must be remembered that there is difficulty in getting true endpoints in titrating a solution which has powdered coal in suspension and that exceedingly accurate determinations could hardly be expected.

Ratios of Hydrochloric Acid to Phosphoric Acid

No.	Direct Treat- ment with P Cl ₅	Blank Test
1.	1.536	1.49
2.	1.515	1.49
3.	1.50	1.48
4.	1.545	1.505
5.	1.535	1.505
6.	1.560	1.51
7.	1.505	1.50

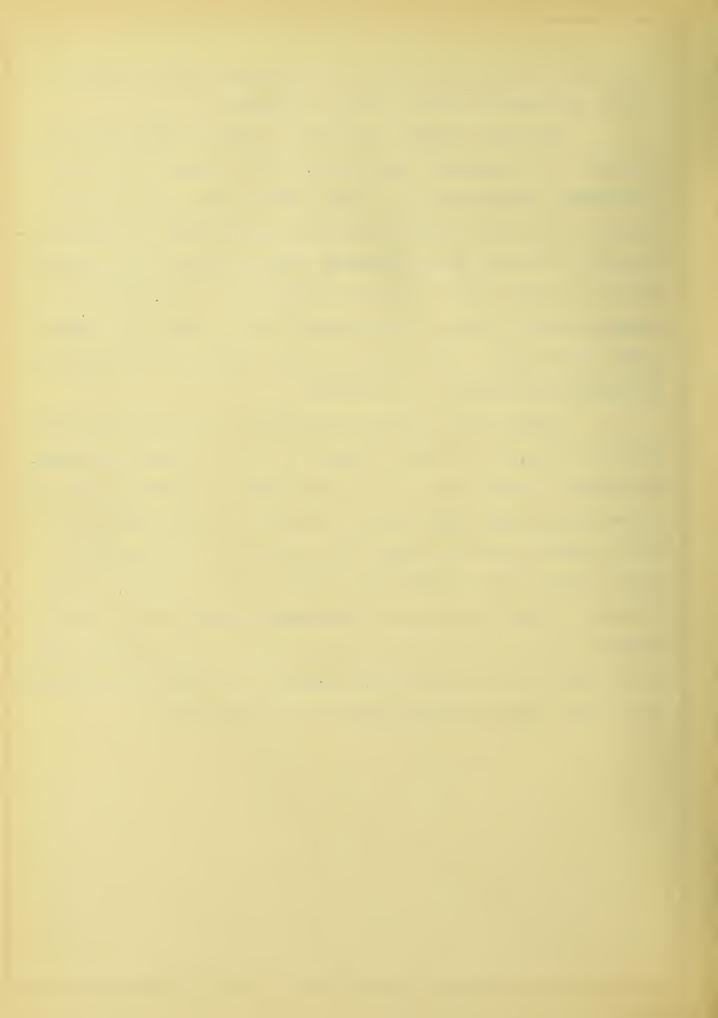
Interpretation of Results. The results of Method 1 (a) cannot be taken as evidence that the hydroxyl group is not present in coal, because the benzoyl chloride mixture has absorbent proper-



ties, and it is possible that all the hydrogen chloride evolved during the reaction would be held in solution.

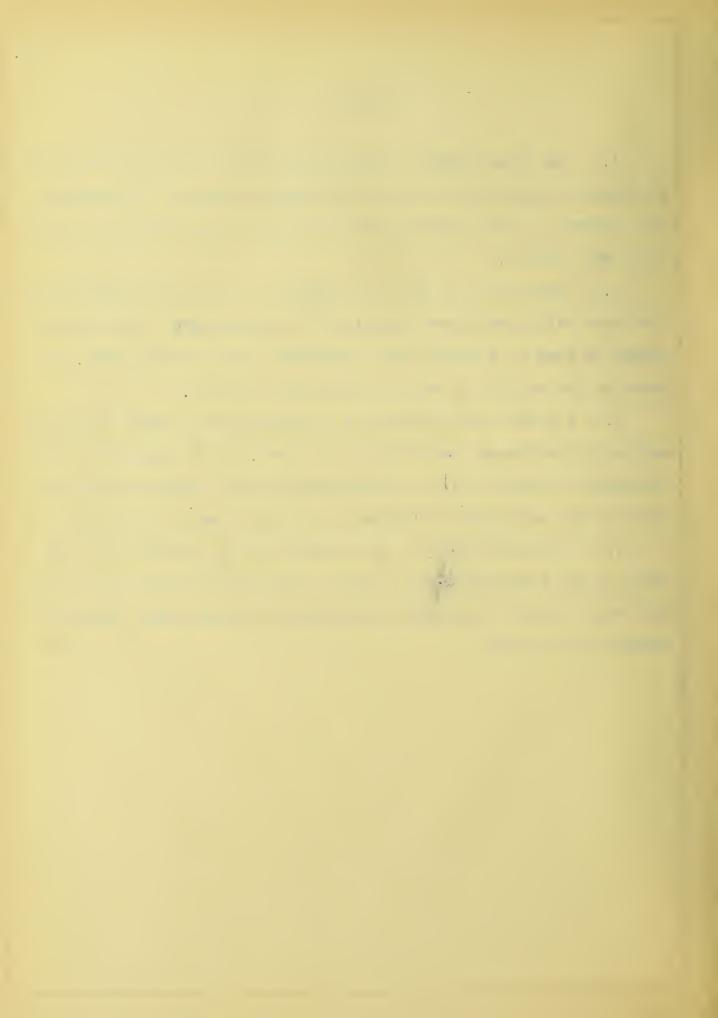
Evidently Method 2 could not be used in determining the presence of the hydroxyl group since, as was shown in the case of phosphorus pentachloride, the coal residue could not be washed entirely free from soluble chlorides. The fact that the coal residue after treatment with phosphorus trichloride in 2 (a) seemed to have been washed free of soluble chlorides may have been due to the method of washing used. When powdered coal is washed in a Büchner funnel with suction, the coal mass forms a cake and it is probable that thorough washing is not effected.

Method 3 as used gave no evidence of the presence of the hydroxyl group, but it does not prove that such a group is absent. One source of error lies in the method used for producing a reaction between phosphorus pentachloride and coal. It is certain that a very intimate mixture of these substances cannot be obtained by merely shaking them together in a flask. It is possible, that by finding a suitable solvent for phosphorus pentachloride, that the reaction could be used as a conclusive test for the hydroxyl group. Future work on the problem should include the design of an apparatus which would insure intimate mixture of the substances.



SUMMARY

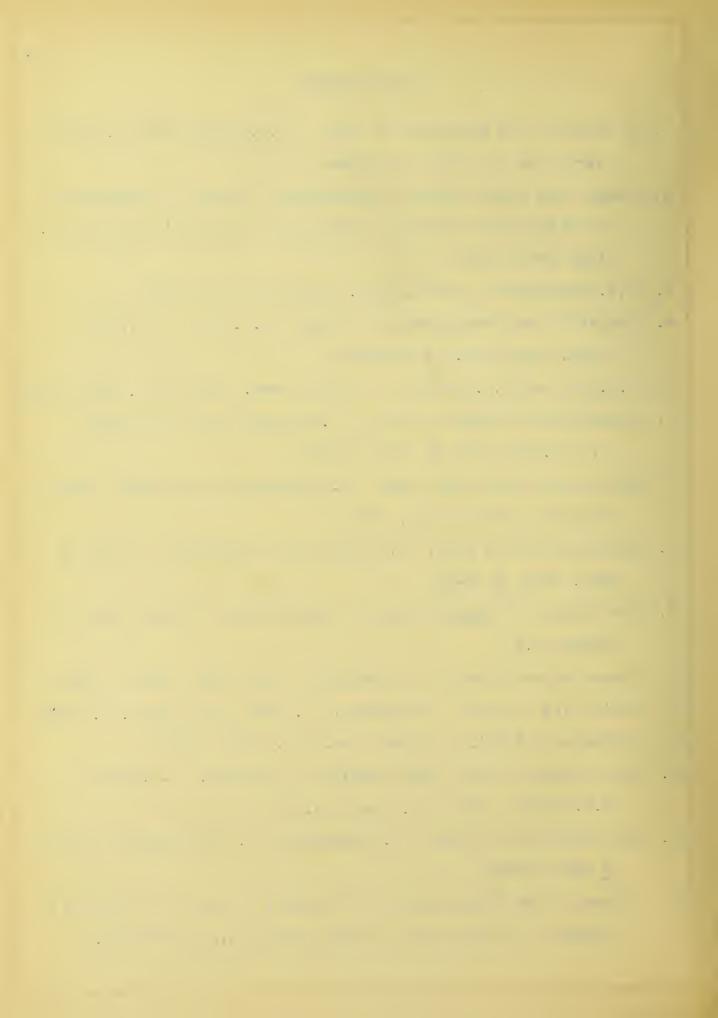
- 1.- The measurement of hydrogen chloride evolved by the action of benzoyl chloride on coal cannot be used as means of determining the presence of the hydroxyl group, because of the absorbent property of the mixture.
- 2.- Examination of the coal residue for chlorine content after treatment with phosphorus trichloride or phosphorus pentachloride cannot be used as a method for determining the hydroxyl group, because of the avidity of coal for hydrogen chloride.
- 3.- A method was devised for determining the extent of the reaction of phosphorus pentachloride on coal, which consisted of the
 titration for hydrochloric and phosphoric acids formed during the
 reaction and subsequent decomposition of the reagent with water.
- 4.- The application of this method did not indicate the presence of the hydroxyl group in coal. This may have been due to the fact that perfect admixture between coal and phosphorus pentachloride was not obtained.



BIBLIOGRAPHY

- 1. A Study of the Oxidation of Coal. H.C.Porter and O.C.Ralston,
 Tech. Pap. 65. Bur. of Mines.
- 2. Ueber eine eigenth#mliche Veranderung, Welche die Steinkohle beim Erhitzen erleidet. E.Richters. Dingler's Polytech.J. 190 398. (1868).
- 3. H.N. Jazukowitsch. Deut. Chem. Zes. Ber. viii 768.
- 4. Oxidation and Deterioration of Coal. A.J.Cox. O.C.Inter. Cong. App. Chem. 10 109-28.
- 5. S.W.Parr and W.F.Wheeler. J. Amer. Chem. Soc. XXX 1, 1028 (1908)
- 6. Absorption of Oxygen by Coal. T.F. Winmill and J.I. Graham.

 J. Soc. Ch. Ind. 33 1000 (1914).
- 7. The Escape of Gas from Coal. H.C.Porter and F.K.Ovitz. Tech.
 Pap. 2. Bur of Mines. U.S.
- 8. Deterioration of Coal. H.C.Porter and F.K.Ovitz. J. Ind. & Eng. Chem. 4 5-8.
- 9. The Effect of Oxygen in Coal. David White. Bull.29, Bur. of Mines, U.S.
- 10. Humus Bodies in Coal. O. Bouduard. Bull. soc. chim. 5 380.
- 11. Humic Acid in Coal. O.Bouduard. J. Chem. Soc. 96 Ai, 12, (1909)
- 12. Bertholet & Andre. J. Chem. Soc. Abs. (1891) 1089.
- 13. The Analysis of Coal with Phenol as a Solvent. S.W.Parr & H.F.Hadley. Bull. 76. Eng. Exp. Sta. U. of I.
- 14. The Weathering of Coal. E. Erdmann and H. Stoltzenburg. Ch. Abs. 3 1585 (1909).
- 15. Errors in the Determination of Moisture in Coal. Hillebrand & Badger. O.C. 8th Inter. Cong. App. Chem. 10 187-190.



- 16. The Action of Air on Coal. P. Mahler. J. Chem. Soc. 98 Aii 607 (1910).
- 17. Powdered Coal Exposed to Air. Taffenel. O.C. 8th Int. Cong.

 App. Chem. 10 277.
- 18. The Spontaneous Combustion of Coal. S.W.Parr and F.W.Kressman

 J. Ind. & Eng. Chem. 3, 151.
- 19. Treadwell-Hall. 3rd Ed. Vol. II. p. 708.





